IB/2004/001055

# *Sertifikaat*

*REPUBLIEK VAN SUID-AFRIKA*

*PATENT KANTOOR*
*DEPARTEMENT VAN HANDEL*
*EN NYWERHEID*

# *Certificate*

*REPUBLIC OF SOUTH AFRICA*

*PATENT OFFICE*
*DEPARTMENT OF TRADE AND*
*INDUSTRY*

Hiermee word gesertifiseer dat
This is to certify that

the documents annexed hereto are true copies of:

Application forms P.1 and P.3 and provisional specification of South African Patent Application No. 2003/2879 as originally filed in the Republic of South Africa on 11 April 2003 in the name of CSIR for an invention entitled: "PACKAGING";

AND it is further certified that an application for amendment was filed at the South African Patent Office on 9 July 2003 to add TRUTER, Patricia-Ann as a co-inventor and the amendment was allowed on 9 July 2003;

AND it is further certified that an application for amendment was filed at the South African Patent Office on 25 March 2004 to delete MKHIZE, Mdusuzi Michael as a co-inventor and the amendment was allowed on 25 March 2004.

**PRIORITY DOCUMENT**
SUBMITTED OR TRANSMITTED IN COMPLIANCE WITH RULE 17.1(a) OR (b)

Geteken te **PRETORIA** in die Republiek van Suid-Afrika, hierdie **29th** dag van **April 2004**

Signed at in the Republic of South Africa, this day of

Registrar of Patents

JBLIC OF SOUTH AFRICA
ENTS ACT, 1978
LICATION FOR A PATENT AND
NOWLEDGEMENT OF RECEIPT
ion 30(1) Regulation 22)

FORM P.1 REVENUE
(to be lodged in duplicate)

11.04.03 ✓ R 060.00

HASR 370
INKOMSTE

GRANT OF A PATENT IS HEREBY REQUESTED BY THE UNDERMENTIONED APPLICANT
THE BASIS OF THE PRESENT APPLICATION FILED IN DUPLICATE

01 PATENT APPLICATION N 2003/2879 ✓ A&A REF V.15690.AS/dcd

FULL NAME(S) OF APPLICANT(S)

CSIR

DDRESS(ES) OF APPLICANT(S)

Corporate Building, Scientia, PRETORIA,
Gauteng Province, Republic of South Africa

4 TITLE OF INVENTION

"PACKAGING"

Only the items marked with an "X" in the blocks below are applicable.

- [ ] THE APPLICANT CLAIMS PRIORITY AS SET OUT ON THE ACCOMPANYING FORM P.2. The earliest priority claimed is
  Country: No: Date:
- [ ] THE APPLICATION IS FOR A PATENT OF ADDITION TO PATENT APPLICATION NO 21 01
- [ ] THIS APPLICATION IS A FRESH APPLICATION IN TERMS OF SECTION 37 AND BASED ON
  APPLICATION NO 21 01

IIS APPLICATION IS ACCOMPANIED BY:

- [X] Two copies of a provisional specification of 13 pages
- [ ] Drawings of sheets
- [ ] Publication particulars and abstract (Form P.8 in duplicate) (for complete only)
- [ ] A copy of Figure of the drawings (if any) for the abstract (for complete only)
- [ ] An assignment of invention
- [ ] Certified priority document(s). (State quantity)
- [ ] Translation of the priority document(s)
- [ ] An assignment of priority rights
- [ ] A copy of Form P.2 and the specification of RSA Patent Application No 21 01
- [X] Form P.2 in duplicate
- [ ] A declaration and power of attorney on Form P.3 - To follow
- [ ] Request for ante-dating on Form P.4
- [ ] Request for classification on Form P.9
- [ ] Request for delay of acceptance on Form P.4
- [ ] Extra copy of informal drawings (for complete only)

74 ADDRESS FOR SERVICE: Adams & Adams, Pretoria

Dated this 11th day of April 2003

AV vR SCHWEIZER
ADAMS & ADAMS
APPLICANTS PATENT ATTORNEYS

The duplicate will be returned to the applicant's address for service as proof of lodging but is not valid unless endorsed with official stamp

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2003 -04- 11
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A&A P201

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TORIA

REPUBLIC OF SOUTH AFRICA
PATENTS ACT, 1978
**DECLARATION AND POWER OF ATTORNEY**
(Section 30 - Regulation 8, 22(i)(c) and 33)

FORM P.3

| ATENT APPLICATION NO | | A&A Ref: V15690 AS/vd | LODGING DATE | |
|---|---|---|---|---|
| 01 | 2003/2879 | | 22 | 11 APRIL 2003 |

| ULL NAME(S) OF APPLICANT(S) | |
|---|---|
| 1 | C S I R |

| ULL NAME(S) OF INVENTOR(S) | |
|---|---|
| 2 | 1. KRÜGER, Arnoldus Jacobus<br>2. MKHIZE, Mduduzi Michael<br>3. TRUTER, Patricia-Ann |

| EARLIEST PRIORITY CLAIMED | COUNTRY | | NUMBER | | DATE | |
|---|---|---|---|---|---|---|
| | 33 | NIL | 31 | NIL | 32 | NIL |

OTE: The country must be indicated by its International Abbreviation - see schedule 4 of the Regulations

| TITLE OF INVENTION | |
|---|---|
| 54 | " PACKAGING " |

I/We **Christopher Robin STURDY**

hereby ~~declare~~ that :-

~~1. I am the applicant mentioned above;~~

2. I/we have been authorized by the applicant to make this declaration and have knowledge of the facts herein stated in the capacity of **Financial Manager** of the applicant(s);

3. the inventors of the abovementioned invention are the persons named above and the applicant has acquired the right to apply by virtue of the provisions of Section 13 of Act 46 of 1988;

4. to the best of my/our knowledge and belief, if a patent is granted on the application, there will be no lawful ground for the revocation of the patent;

* ~~5. this is a convention application and the earliest application from which priority is claimed as set out above is the first application in a convention country in respect of the invention claimed in any of the claims; and~~

6. the partners and qualified staff of the firm of **ADAMS & ADAMS**, patent attorneys, are authorised, jointly and severally, with powers of substitution and revocation, to represent the applicant(s) in this application and to be the address for service of the applicant(s) while the application is pending and after a patent has been granted on the application.

SIGNED THIS 2nd DAY OF July 2003

**For and on behalf of CSIR**
**Full Names of Signatory: Christopher Robin STURDY**
**Capacity of Signatory: Financial Manager**

(no legalization necessary)

* In the case of application in the name of a company, partnership or firm, give full names of signatory/signatories, delete paragraph 1, and enter capacity of each signatory in paragraph 2.
* If the applicant is a natural person, delete paragraph 2.
** If the right to apply is not by virtue of an assignment from the inventor(s), delete "an assignment from the inventor(s)" and give details of acquisition of right.
**** For non-convention applications, delete paragraph 5.

A & A Ref No: **V15690 AS/dcd**

ADAMS & ADAMS
PATENT ATTORNEYS
PRETORIA

FORM P6

REPUBLIC OF SOUTH AFRICA
Patents Act, 1978

# PROVISIONAL SPECIFICATION

(Section 30 (1) - Regulation 27)

| 21 | 01 | OFFICIAL APPLICATION NO |
|---|---|---|

**2003/2879**

| 22 | LODGING DATE |
|---|---|

**11 APRIL 2003**

| 71 | FULL NAME(S) OF APPLICANT(S) |
|---|---|

**CSIR**

| 72 | FULL NAME(S) OF INVENTOR(S) |
|---|---|

**1) KRÜGER, Arnoldus Jacobus**
**2) TRUTER, Patricia-Ann**

| 54 | TITLE OF INVENTION |
|---|---|

**"PACKAGING"**

**This invention** relates to the packaging of goods or substances in packages or containers, in situations where migration of gases, vapours or liquids into or out of the interiors of the packages or containers is undesirable. More particularly, the invention relates to a packaging material for use as a package or container in such packaging of goods, and to a process for producing such packaging material.

According to an aspect of the invention there is provided a packaging material which comprises:

a polymeric base component; and

a barrier component coating and lining a surface of the base component, the barrier component inhibiting migration of gases, vapours and liquids through the base component, and the barrier component comprising a polymeric layer which coats and lines the surface of the base component, the polymeric layer comprising at least two different polar polymer species.

According to another aspect of the invention there is provided a process for producing the packaging material defined above, which process comprises the step of coating a polymeric base component with a barrier component, the barrier

component being in the form of a polymeric layer which coats and lines the base component, and inhibits migration of gases, vapours and liquids through the base component, and the barrier component comprising a plurality of different polar polymer species.

The Applicant is unable to explain the utility of the barrier component, in inhibiting migration of gases, vapours and liquids through the base component, and has found this utility to arise whether the polar polymer species are mixed together, for example in a solution or melt thereof, so that the polymeric layer comprises a mixture, or whether the polar polymer species are present as alternating coatings forming, together, a laminated barrier component. The Applicant is unable to attribute the utility of the barrier component to any interpolymer complexation between the polar polymer species, or any surfactant properties thereof, and it may be that one or more of these mechanisms, or indeed none, is present in the formation of the barrier component.

It will be appreciated that, in the packaging to which the invention relates, the packaging material will be used to form packages or containers for holding or containing goods or substances to be packaged in the interiors thereof, the packages or containers having walls separating the goods or substances in their interiors from the ambient exterior surroundings of the packages or containers, and the inhibition being of the migration of gases, vapours and liquids through the walls

of the packages or containers. It follows that, typically, the packaging material will be in the shape of a package or container; and the process may thus include the step of shaping the base component into a package or container, optionally before the component is coated with the polymeric layer.

When the packaging material is in the shape of package or container, the barrier component may form a coating which lines the inner surface of the package or container, a coating which lines the outer surface of the package or container, or a coating which lines both the inner and outer surfaces of the package or container.

In particular, each of the polar polymer species may be hydrophilic and/or water soluble; and the mixture will usually comprise two said species, although, in principle, more than two species can be employed. The requirement that the polar polymers be of different species means that they must be different with regard to their chemical composition, i.e. differing by more than mere molecular mass or other physical properties.

In a particular embodiment, the polymeric layer of the barrier component may comprise a mixture of the polar polymer species; and in this case the constituents of the mixture of polar polymer species may be combined together, for example by being reacted together such as when the barrier layer is subjected to cross-linking, or they may be caused to interact together, for example to form an interpolymer

complex. Instead, as indicated above, the polar polymer species may form part of a mixture wherein they are not bonded together by either cross-linking or interpolymer complexation, for example when they are mixed solutes in a solution whose solvent evaporates off after the coating step, or when they are constituents of a blend in the form of a melt, which is used to coat the base component. Furthermore, while the barrier component will usually adhere to the base component either by means of van der Waal's forces, such as hydrogen bonding, dipole interaction or the like, or by grafting to the base component to form covalent bonds therewith, neither of these mechanisms need necessarily be present.

When grafting is employed, one or more of the polymer species of the barrier component will be attached to the surface of the base component by covalent bonds, the surface layer provided by the barrier component optionally being semi-migrated or surface-penetrated into the base component. When the surface of the base component is activated as set forth hereunder, free radicals can be created on the surface of the base component, the grafted polymer of the barrier component having molecules bonding to the free radicals on the surface of the base component, although some cross-linking and chain growth may naturally also take place between the molecules of the polymeric species of the barrier component.

When the barrier component is expected to be exposed to abrasion or scuffing, and/or when it is water soluble and is expected to be exposed to moisture,

for example when it forms a coating which lines the outer surface of a package or container, or when it forms a coating which lines the inner surface of a package or container intended to hold an aqueous liquid, the invention contemplates the provision of a protective coating on the barrier component, on the opposite side of the barrier layer, remote from the base component.

With regard to the packages or containers of the present invention, they will typically in use contain goods or substances in the form of solids or, in particular, liquids which can lose constituents thereof to the ambient surroundings or can receive unwanted constituents from the ambient surroundings, by migration of such constituents through the wall of the package or container. The packages or containers will thus usually be in the form of polymeric plastics capsules, sachets, envelopes, jerrycans and, in particular, bottles or jars.

When the goods or substances to be packaged are for human consumption, for example foods, beverages or medicines, the barrier component will usually be intended to inhibit or hinder migration into the package or container of gases from the ambient surroundings, such as oxygen or carbon dioxide, which can have undesired or adverse effects on, and can spoil, the contents of the package or container. Naturally, instead, the barrier component can also resist unwanted loss of constituents to the surroundings, which can similarly devalue said contents. In yet other situations, such as when a jerrycan is intended to contain a hydrocarbon fuel

such as gasoline, diesel or kerosene, or aggressive liquids such as turpentine, paint stripper or thinners, emphasis will be on resisting unwanted migration out of the package or container, of constituents of the contents, through the walls of the package or container, to the ambient surroundings.

The polymeric base component may be of any polymeric material suitable for contact with, and containment of, the goods or substances to be packaged. For example, in the bottling of carbonated beverages such as beer, which is expected to be an important application of the present invention, the coating may line the outer surface of the package or container and the material of the polymeric base component may comprise a polyethylene terephthalate, a polyethylene terephthalate glycol, a polycarbonate, a polystyrene, a polyamide, a polybutylene terephthalate, a polyethelene naphthalate, a polyacrylonitrile, a polymethyl pentene, a polyvinyl chloride, a polyethylene or, in particular, a polypropylene; and copolymers of two or more of the aforegoing can also be suitable.

The species of the barrier layer may in turn be selected from the group consisting of polyvinyl alcohols, polyvinyl amines, polyvinyl imines, polyvinyl acetates, polyglycols, polyacrylic acids, polyalkylacryclic acids, polyacrylamides, polyalkyl acrylamides, polyvinyl pyrrolidones, polylactides, polyanhydrides and polyamides; natural polymers which are celluloses, starches, pectins, proteins and gums, which may be of plant, animal or microbial origin; modified natural polymers which are

hydroxymethyl celluloses, carboxylmethyl celluloses, hydroxyethyl starches, carboxymethyl starches, cellulose acetates, cellulose acetate butyrates, cellulose acetate proprionates and copolymers of any two or more of the aforegoing, a convenient mixture comprising at least one polyvinyl alcohol and at least one polyvinyl amine. Suitable species have been found to be those whose nominal molecular masses are in the range 4000 - 100 000 g/mol, preferably 28 000 - 76 000 g/mol, the major proportion of their molecules falling within these ranges. The mass ratio between the polymeric species of the mixture, for example when there are two species such as a polyvinyl alcohol and a polyvinyl amine, may be in the range 1000:1 - 1:1000 preferably 1000:5 - 5:1000.

While the packages or containers of the present invention can be made by coating the base component with the barrier component and then forming the packages or containers thereafter, as packaging articles, it is expected that, usually, the packaging articles will be formed from the polymer of the base component, after which the coating thereof with the barrier component will take place, optionally on an interior surface, on an exterior surface, or on both interior and exterior surfaces thereof. Coating may be restricted to the exterior surface when the barrier component is water-soluble, and when the package or container is intended to hold contents, such as aqueous contents, which can interact or react adversely with the material of the barrier component.

For enhanced adhesion of the barrier coating to the surface of the base component, the surface of the base component may be activated, by subjecting it to an activating step, prior to the coating step. While the activation step may be physical, for example by roughening or abrading the surface of the base component, or by subjecting it to ultra-violet radiation, gamma radiation, corona discharge treatment, flame treatment, plasma treatment or the like, it may instead be by chemical treatment or etching, such as ozone treatment, fluorine treatment, chlorine treatment, acid treatment, oxidising with a strong oxidising agent such as potassium peroxidisulphate, azoisobutyl nitrile, potassium permanganate or the like, fluorinating and, particularly, oxyfluorinating, being preferred.

More specifically, the activation may be by exposing the base component surface to a fluorine-containing gas mixture containing as little as 0.001% by volume fluorine, preferably >1% and more preferably >5%, the fluorine optionally being admixed with an inert diluent species such as nitrogen, or with a reactive species such as chlorine, sulphur dioxide or, in particular, oxygen, at a reactor pressure of 0.01 - 500kPa, preferably 10 - 300kPa, conveniently 20 - 50 kPa, and at a temperature of 0 - 100°C or more, conveniently at or above ambient, but below the softening point or melting point of the polymeric material of the base component. The temperature will usually be above ambient, because increases in temperature lead to increases in reaction rate. Preferably the activation results in the provision of a surface tension for the activated surface at 20°C of at least 40mN/m, more preferably at least 45mN/m.

For example, the activation may be an oxyfluorination of the type described in United States Patent US 5,900,321.

In a particular embodiment of the invention, coating the base component surface with the barrier component may be by forming a mixture in the form of a solution, for example an aqueous solution, of the constituents or species of the barrier component mixture, and painting or otherwise coating the base component with the solution, followed by removal of the solvent, to dry the coating. When the constituents of the coating are cross-linked, this can be effected by addition of one or more chemical cross-linking agents to the mixture, which agents may be selected from aldehydes such as glyoxal, glutaraldehyde, acetaldehyde or formaldehyde; mineral salts and acids such as boric acid, borax, maleic acid, oxalic acid or hydrochloric acid; isocyanates such as methylene di-isocyanate or toluene di-isocyanate; vinyl compounds such as divinyl sulphates; chromium-containing compounds; and compounds forming redox systems. Cross-linking can instead be effected by physical techniques such as exposure to radiation, which may be selected from one or more of ultra-violet (UV) radiation, electron beam radiation and gamma radiation, or by a combination of chemical and physical techniques. When a protective coating is used to protect the barrier component, for example against water and/or scuffing/abrasion, the material of the protective coating may be selected from polymeric materials such as thermosetting polymers or thermoplastic polymers, examples of which are polyurethanes, polyvinylidine chlorides, polyacrylates,

polyepoxides, polydimethyl siloxanes, and the copolymers thereof or indeed any polymeric material used for the base component, so that the barrier component can be sandwiched or laminated between the base component and barrier component, for example as three layers forming a laminate. In particular polyurethane may be used as the protective coating; and applying the protective coating may be by spraying, dipping, flow-coating, powder-coating, extrusion-coating or vapour deposition.

In tests carried out by the Applicant, the present invention has demonstrated substantial utility in resisting migration through package or container walls of gases such as oxygen, using, on a polypropylene jar base component, a barrier coating comprising a mixture of polyvinyl alcohol and polyvinyl amine, particularly when provided with an outer scuff- and water-resistant coating of polyurethane. In this context, the invention will now be described in more detail, with reference to the following non-limiting illustrative Example.

## EXAMPLE

Polypropylene jars with a volume of 500ml, a wall thickness of 0.55 - 0.85mm, a diameter of 86mm and a height of 83mm were used. The jars were oxyfluorinated by placing them under air at atmospheric pressure in a sealed reactor at 25°C, evacuating the air from the reactor until an absolute pressure of 25 kPa was reached, and injecting a gas mixture comprising 20% $F_2$ and 80% $N_2$ by volume into the

reactor until an absolute pressure of 30 kPa was reached. These reactor conditions were maintained for one minute, after which the reactor was evacuated and flushed with air at atmospheric pressure prior to opening the reactor and removing the jars.

The jars were flow-coated on the exterior surfaces thereof with the compositions shown in the Table set forth below. The coatings were dried in an oven at 60°C for 60 minutes. The bottles were removed and the oxygen transmission rates through the walls of the bottles were determined by flushing pure nitrogen through the bottles and measuring the oxygen contents of the gas streams leaving the bottles with an oxygen detector. The results of these measurements as well as the estimated thicknesses of the coatings are also shown in the Table.

**TABLE**

| Coating Composition | Average Coating Thickness | Average Oxygen Transmission Rate | No of Samples |
|---|---|---|---|
| % | μm | cc/Bottle/Day | |
| None | - | 0.4338 | 6 |
| Water - 90%<br>PVOH - 10% | 8.92 | 0.0281 | 7 |
| Water - 83.4%<br>PVOH - 10%<br>Glyoxal solution - 6.6% | 18.07 | 0.0147 | 9 |
| Water - 83.3%<br>PVOH - 10%<br>Polyvinyl amine solution - 0.1%<br>Glyoxal solution - 6.6% | 14.97 | 0.0045 | 2 |

In the Table PVOH designates polyvinyl alcohol; and the polar polymer species (PVOH and polyvinyl amine) of the barrier coating were cross-linked by means of glyoxal cross-linking agent. No protective coating was employed. The glyoxal solution was a 40% by mass solution of glyoxal in water; and the polyvinyl amine solution was a 50% by mass solution of polyvinyl amine in water. From the Table it can be seen that there is a progressive improvement in barrier properties from the untreated jars through jars coated with polyvinyl alcohol by itself, with polyvinyl alcohol by itself but cross-linked with glyoxal, and finally to a polyvinyl alcohol/polyvinyl amine mixture cross-linked with glyoxal.

**DATED THIS 11th day of APRIL 2003**

**AV vR SCHWEIZER**
**ADAMS & ADAMS**
**APPLICANT'S PATENT ATTORNEYS**